Geology, Genetic Processes And Their Consequences On Environmental Impacts At The Abandoned W Mine Of Enguialès, Aveyron, France

Bruno Lemiere, Jérôme Jacob, Gaël Bellenfant

BRGM, F-45060, Orléans, France

Abstract

We investigate arsenic issues at the Enguialès abandoned tungsten mine, relationships with ore genesis model, hydrogeochemical reactions, and consequences on the environmental impact of the site, and on long-term site management.

Acid runoff was monitored, and waste deposits were mapped using pXRF. AMD generates high As concentrations. Runoff drainage was monitored with a multiparameter probe. Heavy rains followed by strong increases in acidity and conductivity can represent a large proportion of cumulated As discharge.

Continuous EC monitoring is more efficient for transfer evaluation and modelling than periodic sampling. Such data are essential for site management and minimise long-term environmental impacts.

Keywords: Arsenic, tungsten, gravity processing, floatation processing, residues, ARD, AMD, site management

Introduction

We investigate here arsenic issues at the Enguialès abandoned tungsten mine, their relationships with the ore genesis model, and the consequences of the hydrogeochemical reactions on the environmental impact of the site, and on the long-term site management plan.

Geological setting and mining history

The former Enguialès mine belonged to the Leucamp – Enguialès regional tungsten district (Cantal - Aveyron region, French Massif Central), hosted in the pre-Hercynian micaschists sequence of "la Chataigneraie" (Bogdanoff et al., 1987). Basal sericite schists (in green on Figure 1) and greso-pelitic schists (in yellow on Figure 1) are in structural contact but do not differ significantly in mineral or chemical composition. Both are affected by similar metamorphic episodes. This sequence was intruded during Silesian times (Monié et al., 1999) by several types of granites and microgranites. The Entraygues porphyritic monzogranite batholith occurs nearby the mine and probably under it. It has a distinctive contact metamorphism aureole of hornfels and spotted micaschists, with abundant cordierite, poikilitic andalusite, biotite, tourmaline and rare sillimanite. It was intruded by a muscovite leucogranite and by microgranitic veins (Figure 1).

The mineralisation is hosted in a cross-patterned quartz vein stockwork covering 1.3 km × 0.3 km. The recognised extension was 300 m long, with 200 m downwards dip. The mine is located between 400 and 700 m elevation at the surface, across a steep slope above the Lot river valley.

The ore-bearing veins paragenesis comprises quartz, wolframite, scheelite, fluorapatite, while the hydrothermal alteration selvages paragenesis comprises tourmaline (schorl), sericite and sulphides in a quartz greisen. Sulphides come as a first phase (pyrite, arsenopyrite) and a second phase (chalcopyrite, molybdenite, bismuthinite, marcasite), followed by a late carbonate phase. Secondary minerals developed through weathering include oxyhydroxides, hydrated sulphates, and arseniates, the most conspicuous being scorodite.

The vein-type, perigranitic nature, and the structural control result in a high arsenopyrite contents in the veins and their host rocks. Late Variscan leucogranitic magmatism and fluid circulation is believed to be the origin of mineralisation (Lerouge et al., 2000; Goer de Herve et al., 2006).

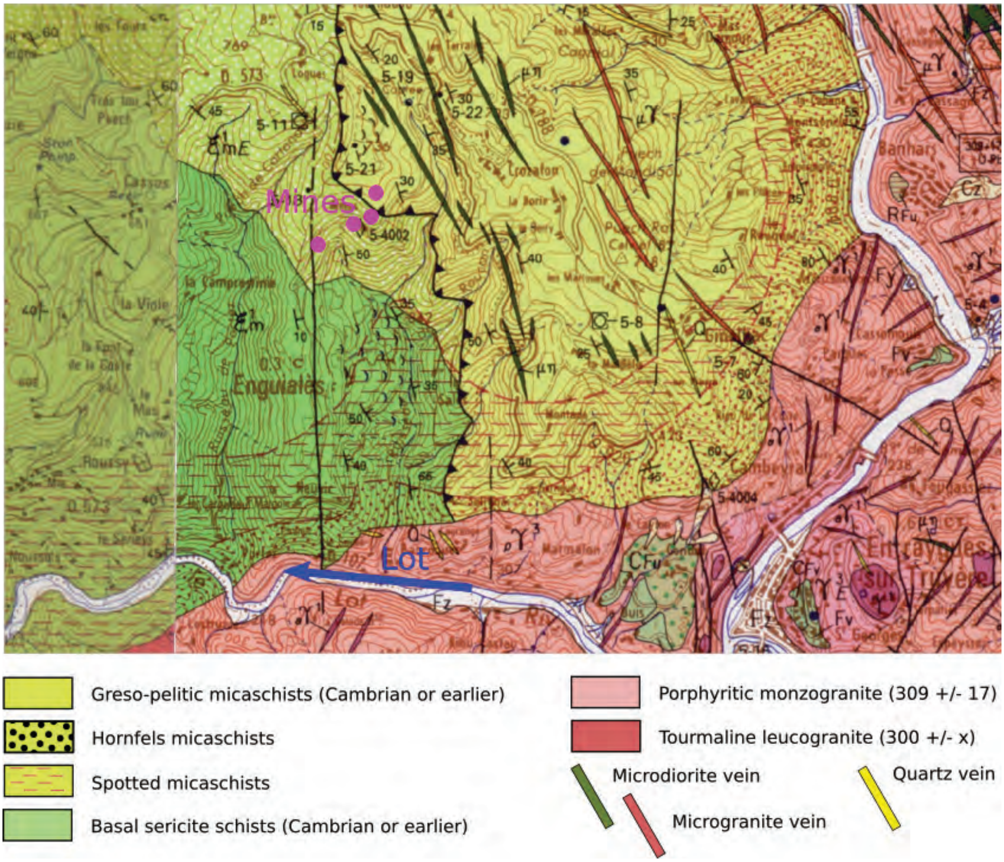

Figure 1: *Geological map (from the 1:50000 map, Goer de Herve et al., 2006) – colours differ slightly between cations and map due to stitching of two map images, see text for disambiguation.*

The deposit was discovered in 1957 and mined from 1969 to 1978. Irregular distribution, recovery and productivity issues, and W price collapse (1971) led to mine closure in 1979. A total 450,000 t of ore averaging 0.6% WO_3 was mined, yielding 1 300 t of 70% WO_3 concentrates.

Ore beneficiation, according to the 1978 flow sheet, comprised crushing and staged milling (size fractions 5mm, 2mm and 0.8mm), pulp preparation, classification, and gravity sorting using jig concentrators or shaking tables. A last concentration step was later added with froth flotation, using mainly gas oil, and then probably specific reagents such as xanthates.

Processing residues comprised therefore +2-5mm gravel, +0.8-2mm dried sand, <0.8mm thickened sand, and sulphidic decantation sludge. Process waste was dumped down the topographic slope out of the galleries. Most waste rock seems to have been used to build platforms and access tracks.

Environmental impacts

The Enguialès mine site is currently managed as abandoned with no responsible party. The first environmental studies were led in connection with EU mining waste inventories (Cottard et al., 2002). The widespread occurrence of As-bearing phases in waste dumps was recognised by Courtin-Nomade et al. (2003) and confirmed by subsequent studies (unpublished data, 2017).

The structural control still applies to site hydrogeology and the faulted network channelizes the As-rich fluids. Pyrite oxidation provided extensive Fe hydroxide coatings. Mining and beneficiation methods determined waste and residues typology. The underground mine opens on a steep topographic slope, on which waste rock and tailings were disposed. A first generation of gravity sorting on coarse mill feed gave moderately reactive quartz tailings, while later finer mill feeds and floatation techniques gave highly reactive and mobile tailings, with much higher As contents. Fast erosion of the latter, accelerated by the steep topography and the intensity of the rainy episodes, contributes to a high As load of surface water in particulate form. Acidic mine runoff is discharged nearby, favouring As and metals solubility, in the absence of any neutralising host rocks traps. Fe hydroxide fracture coatings behave as natural arsenic retardants through sorption phenomena. This reduces groundwater As migration.

Methods

On-site analyses of waste were performed using portable X-ray fluorescence (pXRF) spectrometers. Both soil (Compton) and mining/geochem (fundamental parameters) modes were used in order to cover a large range of elements (As, Ba, Ca, Cr, Fe, K, Mn, Ni, Pb, Rb, S, Sn, Sr, Ti, V, W, Zn, Zr), with 60 to 120 s counting times. Blanks, duplicates and periodic CRMs measurement ensured relative accuracy. Absolute accuracy was evaluated using laboratory analyses, performed by ICP/AES and ICP/MS after acid digestion of alkali sintered samples.

Water analyses were performed on site for physicochemical parameters (pH, ORP, EC) and by laboratory methods (ICP/AES, ion chromatography) for major ions and trace elements.

Water monitoring on site was performed for 49 days in the (TB 465) runoff using an YSI 6920 multiparametric recording probe. The probe was calibrated offsite using standard solutions and checked onsite with an YSI control solution. It recorded hourly pH, temperature, electrical conductivity (EC), redox potential (ORP), turbidity and dissolved oxygen (DO).

The probe was placed in a pipe retained by a dam of stones between the mine drainage spring and a small pond (Figure 2).

Figure 2 : Mine drainage spring (left) and pipe hosting the multiparametric probe (right)

Figure 3 : The probe as recovered (left) and after gentle wiping (right)

Table 1. Results of the verification of the sensors of the probe with standard solutions

Parameter	Unit	Standard solutions	Measured value at 21°C
Conductivity (EC)	µS/cm	1332	1420
pH		4,01	3,6
Redox (ORP)	mV	220	220
Redox (ORP)	mV	470	500
Dissolved oxygen (DO)	%	100	101
Dissolved oxygen (DO)	%	0	21

At the end of the monitoring period, the sensors were checked to evaluate their response to clogging by iron precipitate (Figure 3). The results of this verification are presented in Table 1.

Sensors show a relatively low drift given the important deposits on their surfaces, with the exception of the DO sensor for low concentrations. If the absolute values provided by the probe require a critical reading, their relative variations reflect the events affecting mine drainage.

In order to compare the variations of the mine drainage physico-chemical parameters with precipitation, rainfall data recorded by a nearby (9 km) weather station were used.

Results and discussion

Detailed site investigations by Cottard et al. (2002) and Courtin-Nomade et al. (2003) showed that the main environmental impact of the former mine was As emission towards surface water, resulting from acid drainage out of the mine galleries and from the meteoric leaching of the waste dumps. Dissemination in host micaschists leads also to locally high As concentrations, usually on iron hydroxide coatings that scavenge As from groundwater (Couture et al., 2013).

In order to understand better the origin of acid drainage, the mine runoff was continuously monitored. The mine drainage reaction to short but intense rainfall events was studied. An inventory of the extent of site contamination and of transport modes of the contaminants (both in solute and in particulate form) were carried out.

Solid waste

The process waste deposits were mapped and analysed using pXRF in order to delineate source areas and to establish a preliminary ranking of their hazardousness. This was based on total As only, as no As speciation

Figure 4 *As-bearing coarse gravity sorting residues in dumps (left) - eroded As-rich floatation residues in gravity dumps (right)*

data could be collected. However, the deeply oxidised erosion profile (Figure 4) suggests that, even if the As leachable fraction differs significantly from the total As, the ranking of source areas and the remediation options remain the same.

Two types of residues occur as separate masses along the slope. Coarse-grained quartz-rich material occurs on the outer sides of the dump. It is believed to be the residue of earlier mechanical gravity sorting processes. Their composition is roughly similar to the hydrothermally altered micaschists (Table 2, Table 3) but with anomalously high As and W. They are partly covered by vegetation.

Fine-grained (<1mm) residues occur in the central part of the dump, near the former plant. They are believed to result from later floatation processes with gas-oil and xanthates. A GC/MS scan confirmed the abundance of heavy petroleum hydrocarbons (C10 to C40), did not identify aromatic hydrocarbons but found S-bearing metabolites, probably from xanthates degradation. Their composition is also roughly similar to the hydrothermally altered micaschists (Table 4) but with anomalously high Zn and Cu, and very high As and W. This part of the dump is severely eroded (Figure 4) and carried away to the river, especially during rainstorms. Almost no vegetation grows on this material.

Significant deviations were observed with ICP/AES analyses after aqua regia digestion for Sn, Ti, W, and Zr. For these elements, pXRF results are often more accurate than aqua regia analyses (Lemiere, 2018).

Mine water

Most of the mine drainage is observed as runoff at the TB465 outlet. It is then discharged to a nearby creek and then to the Lot river, 2km downstream. The outlet and the creek were monitored through sampling programs (Cottard et al., 2002, and later unpublished data).

The probe remained in place for 49 days, but iron hydroxide precipitate heavily clogged its sensors. When the probe was recovered, the pipe in which it was placed was completely clogged. Water was no longer flowing through the pipe, but the probe was still in the pond water. Consequently, the recorded values correspond to the physico-chemical parameters of this pond.

Results of conductivity, pH, temperature, dissolved oxygen concentration and rainfall measurements are presented in Figure 5. The ORP sensor seems to have been particularly affected by precipitates, as it hardly recorded

Table 2. *Statistics of pXRF measurements on host micaschists and derived soil, in mg/kg*

	As	W	Mo	Pb	Zn	Cu	Sb	Sn	S	Fe	Mn	Ti	Ca	K	Ba
nb values	19	5	0	15	18	17	15	15	4	20	19	20	19	20	20
mini	16	49		14	32	31	25	32	2723	29015	221	660	307	3929	200
maxi	2034	488		282	225	370	110	100	4076	152090	1659	5855	5355	29311	1633
median	70	112		28	88	101	56	64	3377	49803	594	2606	678	18761	1026
average	325	178		47	92	118	59	63	3388	62831	688	2906	927	17521	969

Table 3. *Statistics of pXRF measurements on coarse residues, in mg/kg*

	As	W	Mo	Pb	Zn	Cu	Sb	Sn	S	Fe	Mn	Ti	Ca	K	Ba
nb values	11	11	6	11	8	10	3	7	4	11	11	11	11	11	11
mini	432	91	9	34	29	37	25	28	1487	32914	212	1886	485	12441	167
maxi	3122	1898	18	134	50	168	35	56	4811	93991	563	3477	1091	24926	579
median	598	366	11	47	36	49	33	34	2649	44522	257	2531	692	17457	401
average	898	464	12	60	38	66	31	38	2899	47254	300	2554	769	18195	398

Table 4. *Statistics of pXRF measurements on fine-grained residues, in mg/kg*

	As	W	Mo	Pb	Zn	Cu	Sb	Sn	S	Fe	Mn	Ti	Ca	K	Ba
nb values	52	52	14	51	30	42	8	35	22	52	50	52	51	52	51
mini	214	153	10	21	31	37	25	18	1296	13473	128	461	319	1872	180
maxi	212336	9423	35	422	1578	6066	73	87	51361	776331	1527	7592	1823	29131	722
median	830	1031	13	57	52	91	36	30	2246	41606	362	2559	699	18357	422
average	11700	1479	16	81	118	445	41	33	8784	86598	420	2654	762	17725	426

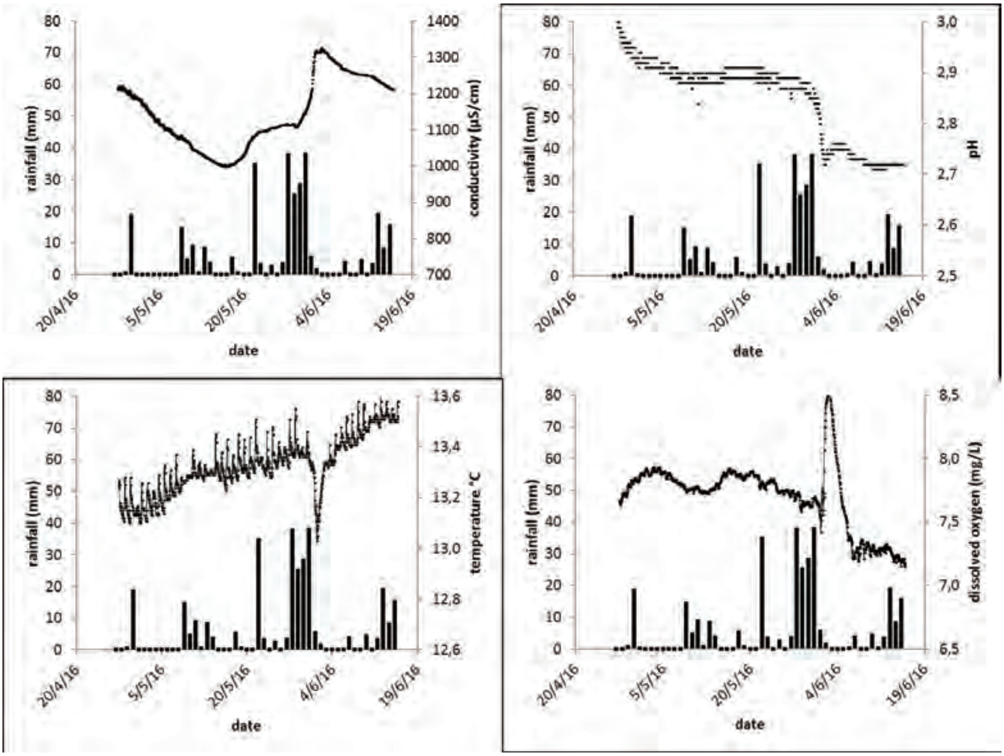

Figure 5 *Conductivity, pH, temperature, dissolved oxygen concentration and rainfall during water monitoring period*

any significant variations. The recorded data are largely unusable and therefore the results of the ORP measurements are not presented.

The monitoring period saw a continuous heavy rain event from May 28 to 31, and an intense but isolated rain event on May 22. The remainder was generally dry with a few days of low rainfall.

EC shows a sharp increase between May 28 and June 1st, followed by a slow decrease until the end of the period. This increase is due to the leaching and dissolution of soluble oxidized minerals in the mine levels above the water table. These minerals were washed during the rain event while they are usually out of the water. pH is globally stable until a sharp acidification episode between May 31 and June 2. This acidification is probably due to the leaching of oxidised sulphides in the mine cavities. When above the water table, they react with air oxygen and with the seepage of oxygenated water. During an intense rain event, they dissolve very quickly, releasing sulphuric acid and soluble metals (Fe, Pb, Zn, etc.).

Water temperature shows a seasonal increase between 13.2 and 13.6°C. Between May 30 and June 2, the temperature drops and then rises sharply, during and after the main rain event. Besides the influx of colder rainwater, it could be due to a decrease in the residence time underground. This is further supported by the time shift between rainfall and temperature change, which would not be observed if the mine aquifer did not play a role.

DO is generally stable except for a sudden increase between May 31 and June 2, followed by a slower decrease until June 6. This increase is probably due to a flowrate drainage increase at the emergence caused by the higher water pressure load due to water inflow. DO variations would therefore indirectly reflect drainage flow variations. DO decrease would represent the progressive drain until the mine returns to its background flow.

Heavy rains were followed by strong increases in acidity and conductivity, As, sulphate and metal contents. The increase in As and metal contents being concomitant with the increase in flow rate, this means that despite their short duration, these events can represent a significant proportion of the As and metal discharge to the environment throughout the year.

Conclusions

The main impact of the abandoned mine is the release of arsenic towards surface water, through process waste erosion and leaching, and through mine runoff. For the former, fine-grained floatation residues are the main source. The steep slopes and the stormy rainfall regime imply that erosion contributes massively to As particular transport, while solute As release could not be precisely located. As leaching is probably active but diffuse. For the latter, water monitoring showed a slowly mitigating As release from the mine runoff but does not allow to investigate in detail the relationships with meteoric events. Continuous monitoring is more efficient for transfer evaluation and modelling than periodic sampling. Such data are essential for site management and to minimise long-term environmental impacts.

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